COATINGS. ENAMELS

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NO-UNDERCOAT ENAMELS WITH A COMPLEX BONDING CATALYST FOR PUESTA TECHNOLOGY

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The effect of the composition of enamel frits containing a complex bonding catalyst on the resistivity and adhesion of frit powders to low-carbon steel and the coating – metal bonding strength is studied. It is determined that low-melting competitive no-undercoat enamels for the PUESTA powder electrostatic coating deposition technology with a complex bonding catalyst containing the minimum amount of expensive bonding oxides NiO and CoO with firing temperature 780 – 800°C can be synthesized. The composition of the no-undercoat frits for the PUESTA technology adopted for home appliances is developed.

Key words: no-undercoat glass enamels, catalysis for bonding with metal, PUESTA technology, lower of the firing temperature.

The present growth in the production of enameled home appliances, specifically, electric and gas stoves, is encountering problems of energy and resource conservation and increasing the environmental acceptability of the production process as a whole. The PUESTA powder electrostatic enameling technology makes is possible to obtain high-quality competitive products. It is largely this technology that gives environmental acceptability, waste-free production, and minimal energy consumption in the production process [1]. However, special glass-enamel frits with complicated properties, making it possible to deposit fine enamel powders in a high-voltage field, are required to implement this technology.

Since domestic enterprises are converting to European standards for the production of enamel frits, powders, and coatings the limitations on the content of fluorides, Mo, Ba, and Zn compounds, and nickel oxide, which is one of the main bonding oxides together with cobalt oxide, must be taken into account when developing new compositions for enamels [2]. It is important to note that the cost of the conventional bonding oxides NiO and CoO in the undercoat and no-undercoat darkly colored enamels ranges from 45 to 70%; their total content ranges from 1.5 to 3%.[3]

The purpose of the present work was to develop the compositions of competitive, low-melting, undercoat-free enamels for the PUESTA technology of powder electrostatic deposition using a complex bonding catalyst (CBC), containing minimal amounts of the expensive bonding oxides NiO and CoO. The complexity lay in the need to ensure the bonding strength between the no-undercoat enamel and a steel base firing temperature 780 – 800°C, which is unconventionally low for enamel articles made of thin steel.

The need to take account of the economic aspect, specifically, the cost of the enamel frit based on the raw materials must be less than the world market prices for similar special frits, complicates the solution of the problem. The expensive items in the compositions of low-melting enamels for the PUESTA technology are lithium-containing compounds, whose cost is 8 – 16% of the cost of all raw materials in the enamel mix. In this connection the possibility of synthesizing lithium-free enamel frits, which would reduce the price of the final product considerably, was investigated in the present work.

Previously, we developed a CBC which contained 1 – 1.5% nickel oxide [3]. This bonding activator was introduced into undercoat enamels with firing temperature 810 – 830°C for the coatings made from them. Taking account of these limitations, the concept of synthesizing low-melting glass-enamel frits forming high-corrosion-active melt in the temperature interval 780 – 810°C was advanced. This should give an intense interaction of the glass-enamel melt with the steel base and give a protective coating with bonding strength 4 – 5 on the GOST 24405–80 scale or 1 – 2 on the EN 10209 scale.

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[3] Here and below, unless otherwise state, content by weight.

TABLE 1. Compositions of Experimental Frits

Frit	Content, wt.%									
	SiO_2	B_2O_3	Al_2O_3	RO_2	R_2O	RO	CBC		CaF_2	P_2O_5
							CoO + NiO + CuO	$MnO_2 + Fe_2O_3$		
DM 36*	30.9	20.0	–	2.0	26.5	6.0	1.6	5.0	4.0	2.0
DM 39	32.0	19.0	–	2.0	28.0	5.0	1.5	5.0	3.5	4.0
DM 40*	32.4	20.0	–	2.0	28.5	5.0	1.6	5.0	3.5	2.0
DM 9	45.0	13.0	–	1.5	23.0	8.0	1.8	3.7	4.0	–
DM 45*	43.5	27.0	2.0	–	13.0	5.5	1.5	4.0	3.5	–
DM 48**	40.3	17.0	8.0	–	20.0	5.6	1.2	0.6	4.0	–
DM 49**	50.3	26.1	2.2	–	12.9	1.1	1.2	1.2	5.0	–
DM 51**	48.1	12.0	5.0	–	18.5	10.0	1.2	1.2	4.0	
DM 58**	49.5	20.0	3.0	–	14.0	4.0	1.0	4.5	4.0	–
DM 59	49.5	20.0	3.0	–	14.0	4.0	1.3	4.5	3.7	–

Notations: $R_2O_3 = B_2O_3 + Al_2O_3$; $R_2O = Na_2O + K_2O + Li_2O$; RO = CaO + BaO.

* Nickel-free compositions.

** CuO-free compositions.

On this basis the composition of the bonding catalyst for undercoat enamels for the PUESTA technology was systematically varied and expanded by adding compounds which increase the reactivity of the melt: MnO_2, Fe_2O_3, and CuO. The low-melting property of the enamel frit was increased at the same time while keeping its high resistivity $\rho \geq 10^9\ \Omega \cdot m$, which the particulars of the PUESTA technology make necessary.

The investigations led to the development of a series of experimental compositions (> 50) of low-melting, glass-enamel, no-undercoat, dark-colored frits DM. Table 1 shows some compositions for frits in this series, including DM 9, DM 36, DM 39, and DM 40, containing up to 1% Li_2O; all others are lithium-free.

Two main directions of synthesis of the low-melting glass-enamel first were used in this work. The first one is the development of multi-alkali compositions with content $\Sigma(Na_2O + K_2O) = 20.0 – 28.0\%$; the second one is the development of multi-boron compositions with B_2O_3 content from 18.0 to 28.0%.

The manifestation of the polyalkali effect was used in the first and second series of composition DM to ensure high resistivity $\rho \geq (1 – 9) \times 10^{10}\ \Omega \cdot m$ ($\log \rho_{20} \geq 10$) due to the introduction of alkali oxides Na_2O and K_2O in the ratios 5 : 1 and 4 : 1 and alkali-earth oxides CaO and BaO in the ratios 2: 1 and 3 : 1 (compositions are expressed in molar percent). The polyalkali low-silica compositions, specifically, DM 36, DM 39, and DM 40, with total content of the alkali oxides 26.5 – 28.5% were characterized by high resistivity ($\log \rho_{20} \geq 11$) owing to the definite ratio of the active cations $Na^+ : K^+$ and $Ca^+ : Ba^+$.

The lowest values of the resistivity $\log \rho_{20} \sim 9.0$ are observed for the frits DM 48 and DM 51, to whose compositions alkali oxides were introduced only due to Na_2O and alkali-earth oxides only due to CaO, and the complex bonding catalyst did not include CuO and Fe_2O_3. To eliminate any effect due to the surface conductivity χ_s on the value of the electric resistance of glass powders it was determined in a regime of heating to 200°C — cooling to 20°C. The value obtained for the resistivity ρ of fine powders of the experimental enamel glass-frits after heating to 200°C and cooling to 20°C confirmed the total polyalkaline and polycationic effects — suppression — in the synthesized compositions on their electric properties (Table 2).

The highest values of the resistivity were observed for powders (no encapsulation) of the frits DM 36, DM 58, and DM 59. Powders of these frits encapsulated by hydrophobic

TABLE 2. Value of $\log \rho_{20}$ for the Experimental Frits

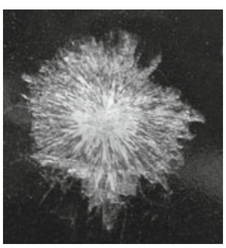
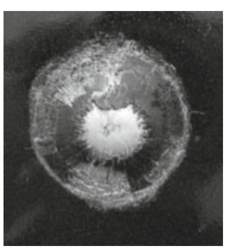
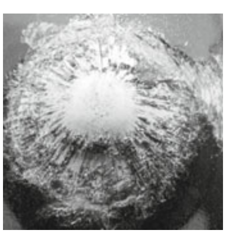
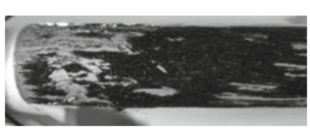
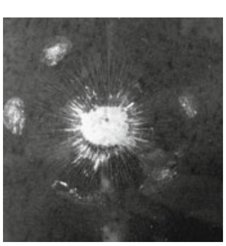
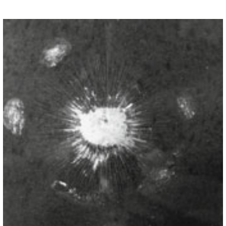
Values of $\log \rho_{20}$	Frit									
	DM 36	DM 39	DM 40	DM 9	DM 45	DM 48	DM 49	DM 51	DM 58	DM 59
Before heating	7.1	6.8	6.80	5.3	6.6	6.2	5.90	5.1	6.9	7.2
After cooling	12.3	11.1	11.17	10.0	11.4	9.2	10.55	9.0	11.7	11.6

TABLE 3. Bonding Strength of the Experimental Coatings on EK-2 Steel

Coat bonding strength, scale value	Frit									
	DM 36	DM 39	DM 40	DM 9	DM 45	DM 48	DM 49	DM 51	DM 58	DM 59
GOST 24405 impact	4 – 5	4	3 – 4	4 – 5	4 – 5	3 – 4	3 – 4	3 – 4	4 – 5	4 – 5
EN 10209 impact	1 – 2	3	2 – 3	1 – 2	1 – 2	2 – 3	2 – 3	2 – 3	1 – 2	1 – 2
GOST 24788 bending	4 – 5	4	3 – 4	4 – 5	4 – 5	3 – 4	3 – 4	3 – 4	4 – 5	4 – 5

organo-silicon films showed electrostatic adhesion to steel samples $A = 85 – 87\%$.

TABLE 4. Post-Testing Exterior Appearance of Enameled Samples

Frit	Post-testing appearance of sample	
	under impact	under bending
DM 39		
DM 40		
DM 48 DM 49		
DM 58		
DM 9 DM 59		

The second very important property for uncoated coatings on thin-sheet low-carbon steels is the bonding strength. This indicator was determined on enameled samples of EK-2 steel fired in the temperature interval 780 – 810°C for 4 min. Such values of the firing temperature and time for the coatings are due to the technological particulars of the equipment and the specific nature of the production of the enameled home appliances from thin-sheet steels on automated lines. The measurements of the bonding strength were performed under impact and bending in accordance with the operative requirements for enamel coatings — GOST 24405 and GOST 24788, EN 10209. The results of the determination are presented in Tables 3 and 4.

As the data presented show, the DM9, DM 36, DM 45, DM 58, and DM 59 coatings were characterized by high bonding strength with EK-2 steel; but, expensive lithium-containing polyboron frits were used to obtain the coatings DM 9 and DM 36. The optimal firing temperature of a coating was 830 – 840°C, which is much higher than required. The polyboron coating DM 45 was characterized by the presence of pores and the absence of sheen. In addition, the coating DM 9 has a bluish tinge.

The compositions DM 58 and DM 59 were characterized by a deep black color due to the established content and ratio of the variable-valence metal oxides. This factor in combination with the high degree of adhesion of the powders having the indicated compositions, strong bonding of the coatings with low-carbon thin-sheet steel EK-2, and the least expensive frit determined their choice for commercial use in the production of home ranges.

So, it has been determined that low-melting competitive coating-free enamels for the powder electrostatic deposition technology PUESTA with a complex bonding catalyst (CBC), containing a minimum amount of expensive bonding oxides NiO and CoO, with firing temperature 780 – 800°C can be synthesized.

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